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THERMOANALYTICAL TECHNIQUES APPLIED TO THE ANALYSIS OF AN ITALIAN SOFT CHEESE: A CRITICAL COMPARISON WITH THE OFFICIAL METHODS OF ANALYSIS

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ABSTRACT

A study concerning the possibility of using thermoanalytical techniques for the determination of water and ashes in cheese has been carried out in comparison with the official methods of analysis. A soft Italian cheese, fiordilatte (a kind of mozzarella cheese), has been studied.

Seven different brands including those most widely available have been analysed by both methods and the results were compared and discussed. The discussion has been supported by dehydration kinetic studies. Finally, the ageing of the cheese has been studied and discussed.

INTRODUCTION

The official procedures adopted for cheese analysis are founded on operating principles which are sometimes empirical and often complicated and time consuming.

The official method for the determination of water [1] requires that the analysis be carried out on 5 g of cheese. For hard paste cheeses it is possible to use a capsule directly, while for soft paste cheeses it is necessary to mix the weighed sample, using a glass rod, with washed and calcined sand. In this case the sample is weighed directly in a previously calibrated capsule together with the sand and the glass rod. The drying process is then carried out in an oven at 102°C to constant weight. For very humid cheeses, it is advisable to dry the sample for at least six hours in a sulphuric acid

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desiccator at room temperature before putting it in the oven. The drying temperature and the drying time are obviously the critical parameters of the analysis.

The selection of 102°C is obvious because it is near the boiling point of water and so, under these conditions, the vapour pressure would be sufficiently high to effect complete removal of the water. Nevertheless, it has been widely proved that water, including that in biological systems, is often bound to other components of the system by hydrogen bonds, van der Waals forces, etc. The bound water, according to Watterson [2], takes part in mutual interaction on a macromolecular scale. This results in clusters having a relatively long-term existence, which strongly stabilize the water molecules. In order to reach an activation energy suitable to release the water, temperatures higher than 100°C could be needed. In addition, the operational times of the official methods are quite long.

Therefore, the possible use of instrumental techniques, such as thermoanalysis, was considered. Moreover, thermal analysis offers the advantage that all the thermal decomposition trends of the sample can be observed, thus yielding information on the other components of the system. Finally, it is also possible to determine the ashes of the sample. The official methods also provide for ashes analysis but include very long operational times, a muddled procedure, critical ashing temperatures, etc.

The aim of this paper is to investigate the possibility of using thermoanalytical techniques as a new tool for the determination of some of the analytical parameters of cheese. The first problem considered has been the application of thermal analysis to the determination of water and ashes in an Italian soft cheese, fiordilatte (a kind of mozzarella cheese), using a comparison between the thermal analytical techniques and the official methods of analysis.

EXPERIMENTAL

Instrumentation

A Perkin–Elmer model TGS-2 thermobalance equipped with a data station was used. The heating rate ranged between 10 and 40°C min^{-1} and the atmosphere was air or oxygen at a flow rate of 50–100 ml min^{-1}. Other apparatus included analytical balance from Mettler, a muffle, an oven and a water bath.

RESULTS

To compare the analytical data obtained by the thermoanalytical techniques and by the official methods of analysis, all the fiordilatte samples,

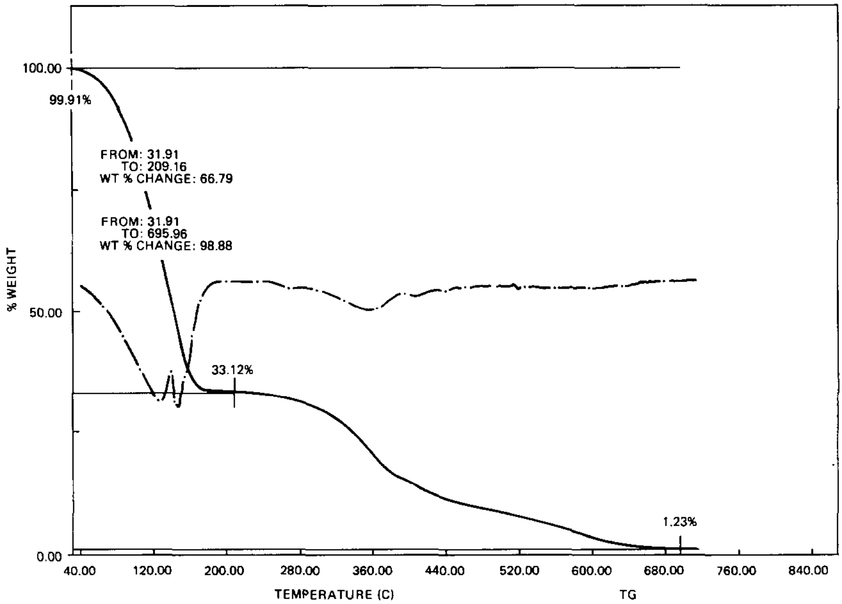

Fig. 1. Thermogravimetric curve of fiordilatte sample A, heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

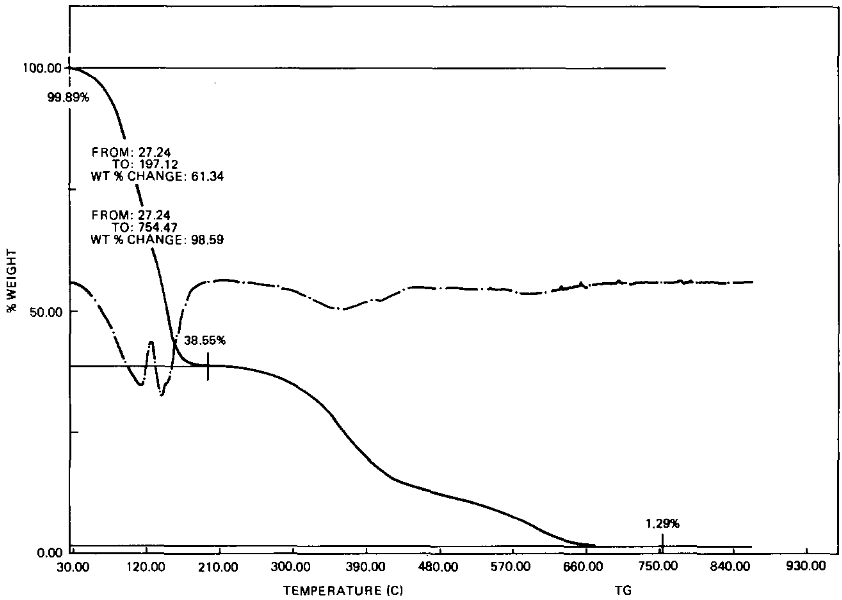

Fig. 2. Thermogravimetric curve of fiordilatte sample B, heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

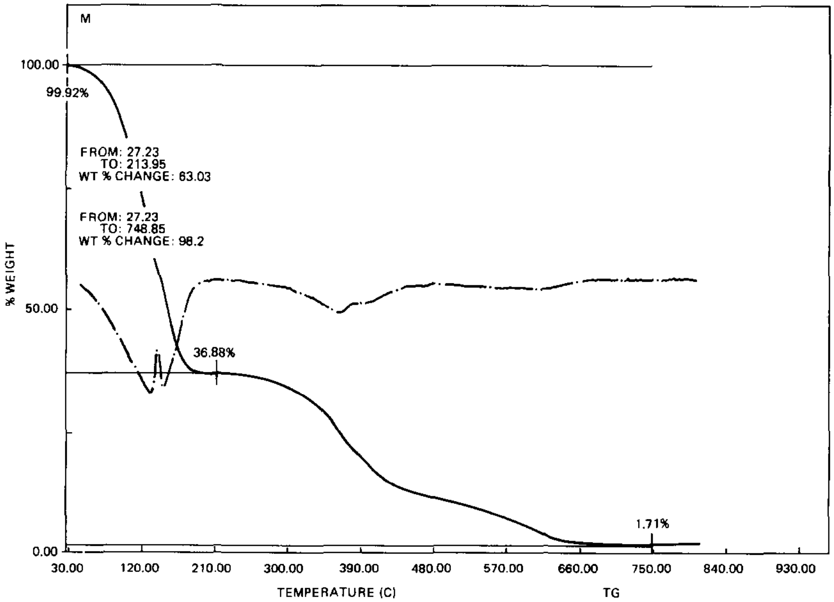

Fig. 3. Thermogravimetric curve of fiordilatte sample C, heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

purchased in the supermarkets, were analysed in parallel, sampling by a probe and working so that the samples for both the analyses were as similar as possible.

Samples were collected and stored according to the official directions and were always analysed 2 days after manufacture; distribution problems make analysis after one day impossible.

Fiordilatte samples of seven different brands including those most readily available were chosen. The samples were marked by the letters A–G.

Figures 1–7 show, as an example, one thermoanalytical curve for each of the analysed samples. The thermogravimetric curves show that each time the water loss occurs via two partially overlapping processes, in the temperature range 30–220 °C.

The dry cheese then decomposes through three different steps, the first two, partially overlapping, ranged between 300 and 450 °C while the third is situated at higher temperatures. Then, in the range 650–680 °C, at the heating rate of 10 °C min^{-1}, the ashes are obtained.

To compare the thermoanalytical and the official methods, ten samples, of each one of the seven studied brands, were analysed for water and for ashes by the two different analytical techniques. The results are listed in Tables 1 and 2.

Analyses were also carried out at 20 °C min^{-1} and at 40 °C min^{-1}. The results obtained were exactly the same as those obtained at 10 °C min^{-1}.

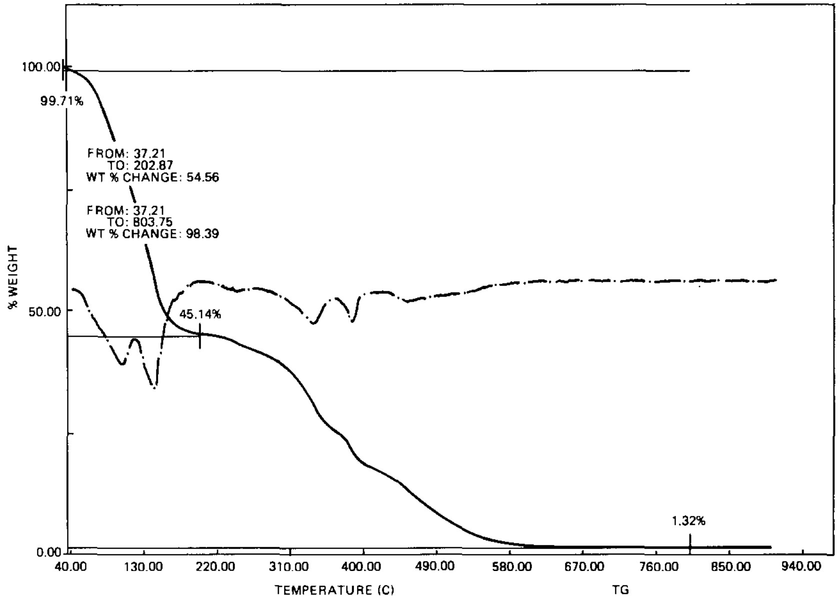

Fig. 4. Thermogravimetric curve of fiordilatte sample D, heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

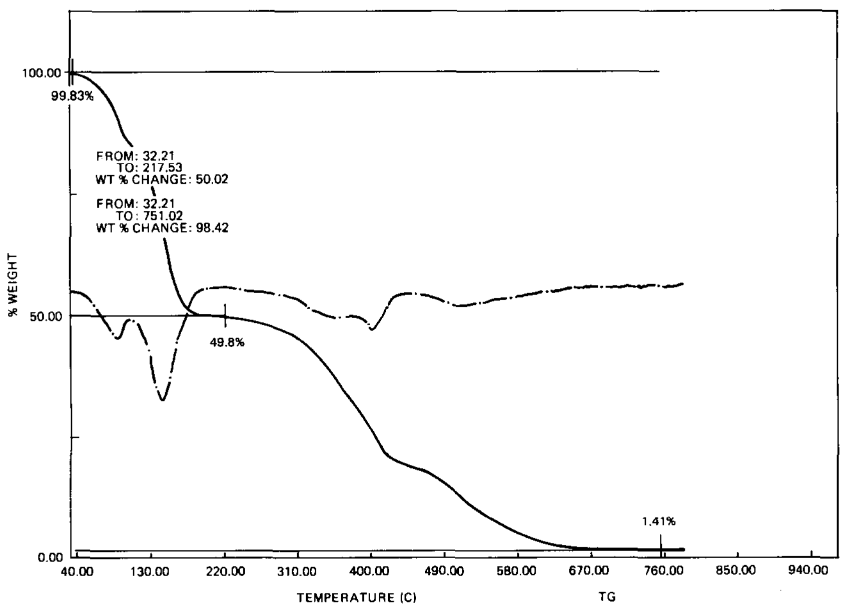

Fig. 5. Thermogravimetric curve of fiordilatte sample E, heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

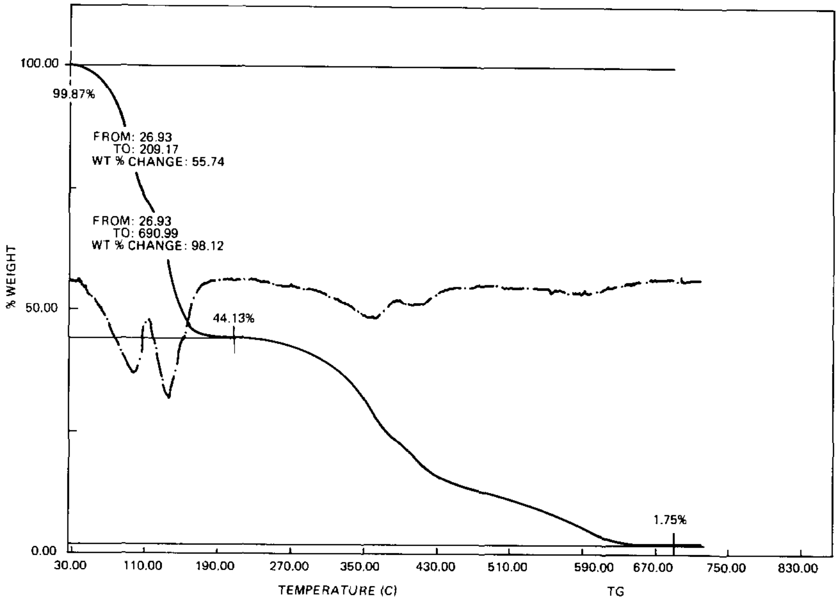

Fig. 6. Thermogravimetric curve of fiordilatte sample F, heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

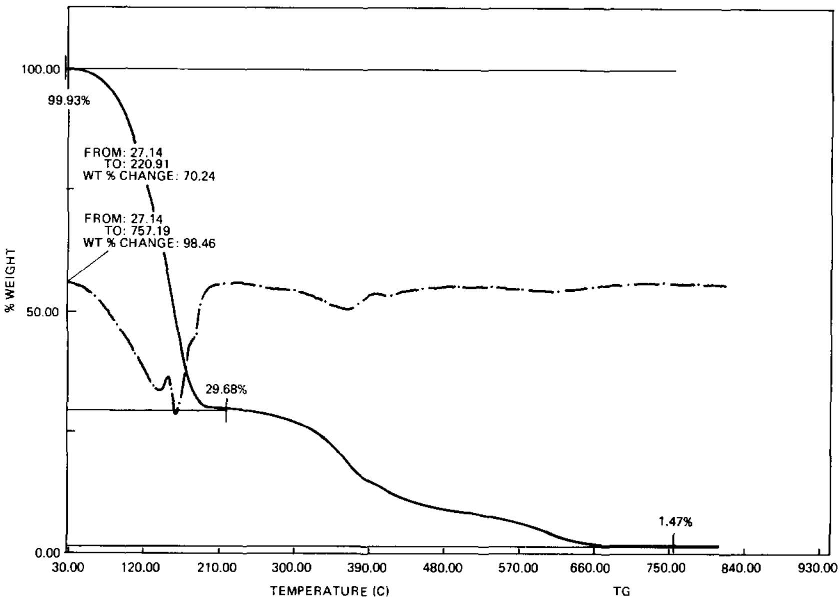

Fig. 7. Thermogravimetric curve of fiordilatte sample G, heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

TABLE 1

Analysis of water, expressed as a percentage of the total weight of the sample, obtained by the official method and by the thermoanalytical method. Uncertainty is given as the standard deviation of ten different analyses

Sample	Official method	Thermogravimetry
A	56.0 ± 2.8	62.4 ± 1.4
B	57.1 ± 2.6	58.5 ± 1.6
C	58.1 ± 2.4	60.4 ± 1.4
D	56.1 ± 2.6	56.8 ± 1.7
E	44.5 ± 1.9	48.6 ± 1.2
F	55.9 ± 2.1	57.7 ± 1.4
G	67.6 ± 3.1	70.2 ± 1.8

As can be seen, the TG results for the water are always higher than those obtained by the official methods. To explain this trend, the dehydration kinetics have been studied.

A 100 g sample of one of the studied brands of fiordilatte was obtained following official directions. The sample was then divided into 20 homogeneous 5 g subsamples which were each placed in a capsule.

One sample was immediately analysed by TG (Fig. 5), while the others were placed in an oven at 102°C. Then, every hour, one sample was removed from the oven and analysed by TG, each sample, about 50 mg, being taken from the centre of the mass. The results are shown in Figs. 8 and 9. The edge of the mass of the 12 h sample was also analysed (Fig. 10).

The kinetic study was repeated two further times on samples of the same brand with the same results. Then, samples of the other brands were kinetically studied with similar results.

Kinetic studies carried out at an oven temperature higher than 102°C show that the water is totally released in shorter times as the oven tempera-

TABLE 2

Analysis of ashes, expressed as a percentage of the total weight of the sample, obtained by the official method and by the thermoanalytical method. Uncertainty is given as the standard deviation of ten different analyses

Sample	Official method	Thermogravimetry
A	1.65 ± 0.09	1.88 ± 0.05
B	1.60 ± 0.08	1.91 ± 0.04
C	1.80 ± 0.10	1.83 ± 0.04
D	1.90 ± 0.09	2.16 ± 0.03
E	1.67 ± 0.09	1.74 ± 0.04
F	1.81 ± 0.08	1.93 ± 0.05
G	1.40 ± 0.09	1.47 ± 0.04

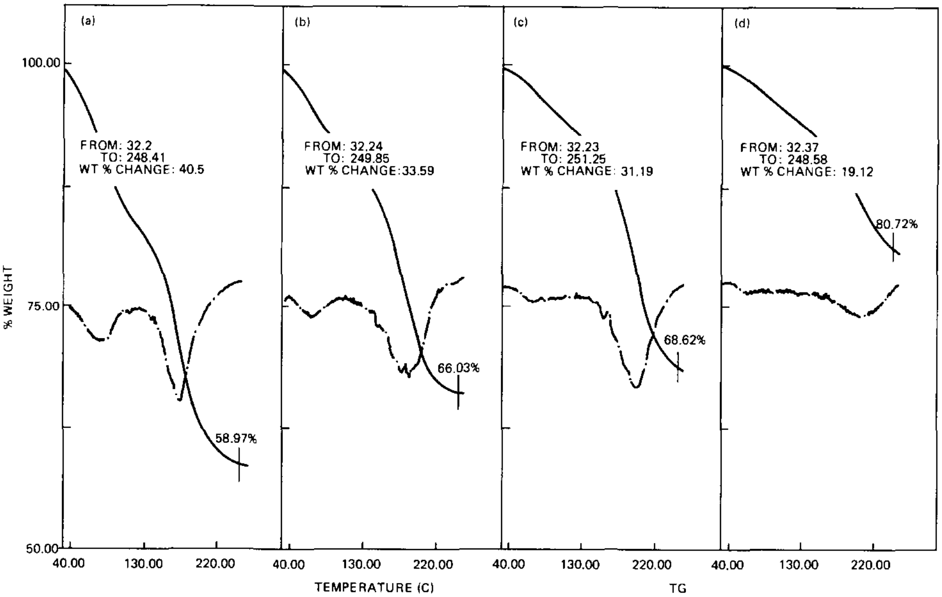

Fig. 8. Thermogravimetric curves of fiordilatte sample E after different periods in the oven at 102° C, TG samples removed from the centre of the mass: a, 1 hour; b, 2 hours; c, 3 hours; d, 4 hours. Heating rate 10° C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

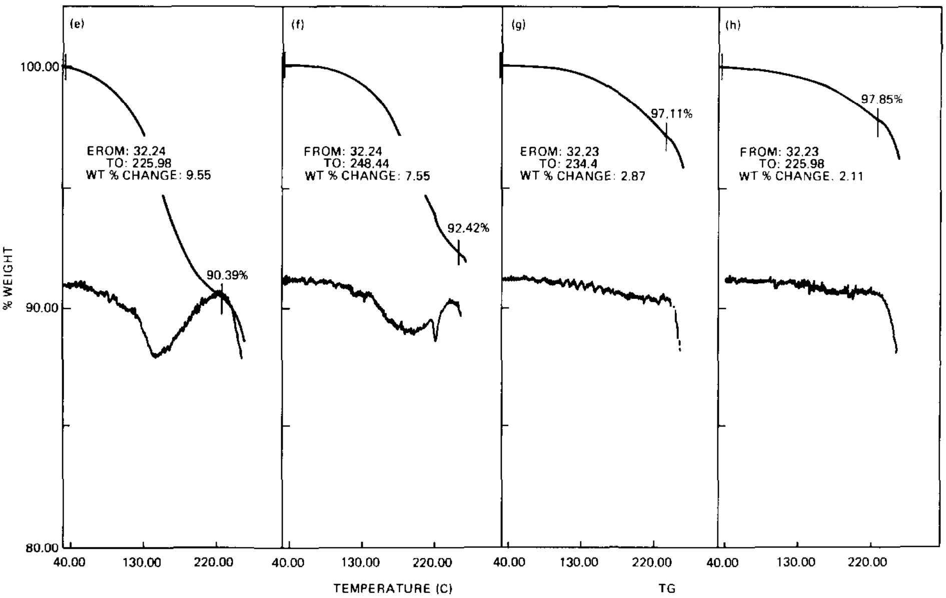

Fig. 9. Thermogravimetric curves of fiordilatte sample E after different periods in the oven at 102° C, TG samples removed from the centre of the mass: e, 6 hours; f, 8 hours; g, 10 hours; h, 12 hours. Heating rate 10° C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

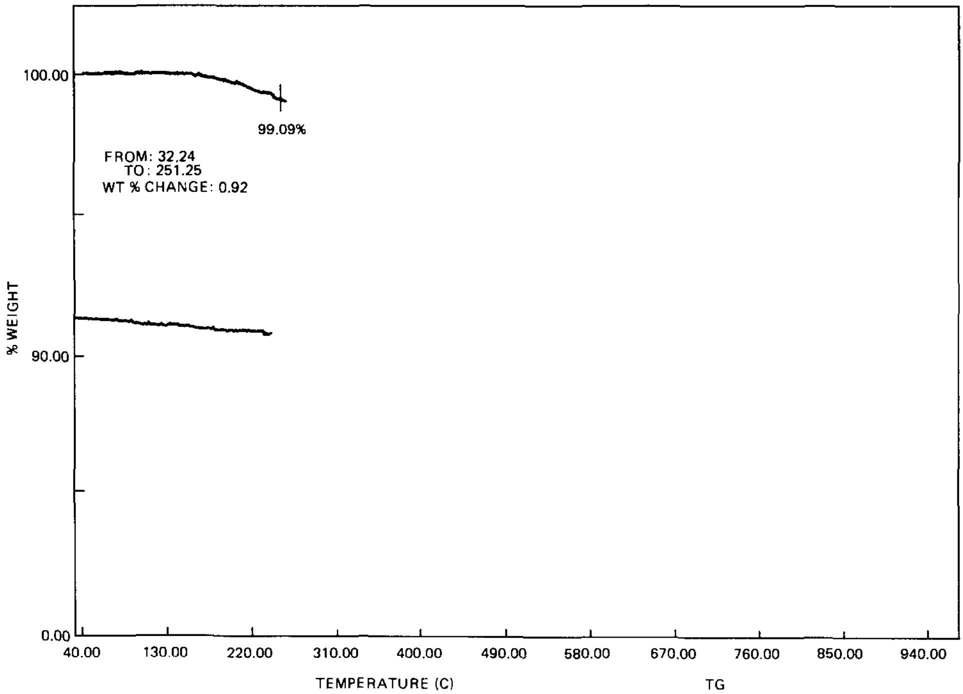

Fig. 10. Thermogravimetric curve of fiordilatte sample E after 12 hours in the oven at 102 °C, TG sample removed from the edge of the mass. Heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

ture increases, but at the same time the decomposition of the dry cheese begins, thus giving incorrect results.

Finally, the ageing of the fiordilatte was studied on samples stored according to the official directions. The ageing was followed by thermogravimetric analysis with a special interest in the water behaviour. Figures 11 and 12 show, as an example, the thermoanalytical curves corresponding to

TABLE 3

Thermogravimetric analysis of water in a sample of fiordilatte after different numbers of days

Days	Total water	Unbound water	Bound water
2	66.79	46.61	20.18
3	61.15	38.20	22.95
4	57.72	33.28	24.34
5	58.10	32.22	25.88
6	58.04	30.74	27.30
7	57.92	29.82	28.10

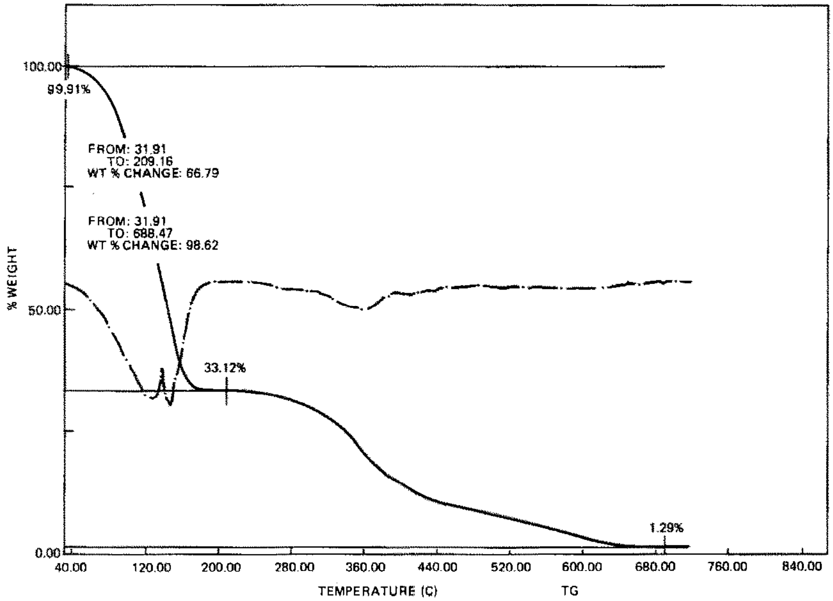

Fig. 11. Thermogravimetric curve of fiordilatte sample A at 2 days after manufacture. Heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

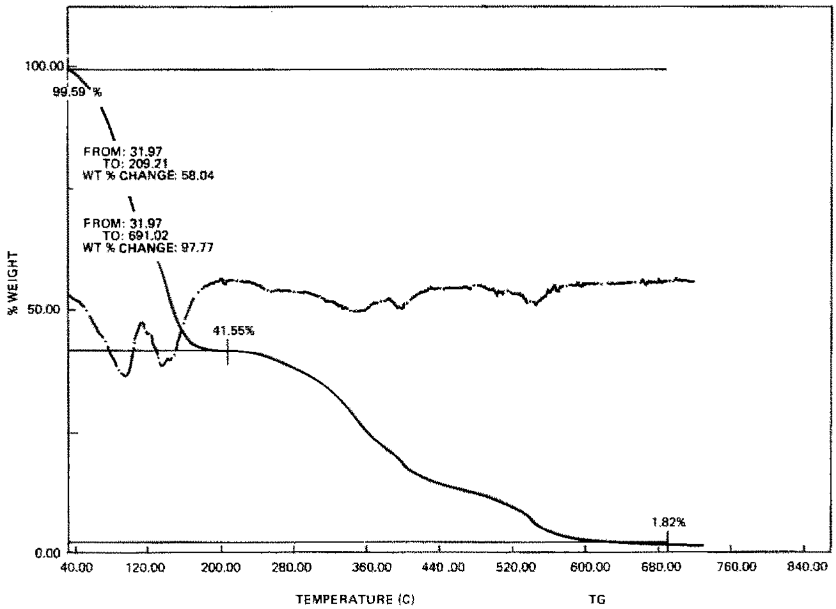

Fig. 12. Thermogravimetric curve of fiordilatte sample A at 6 days after manufacture. Heating rate 10 °C min^{-1}, atmosphere oxygen at a flow rate of 100 ml min^{-1}.

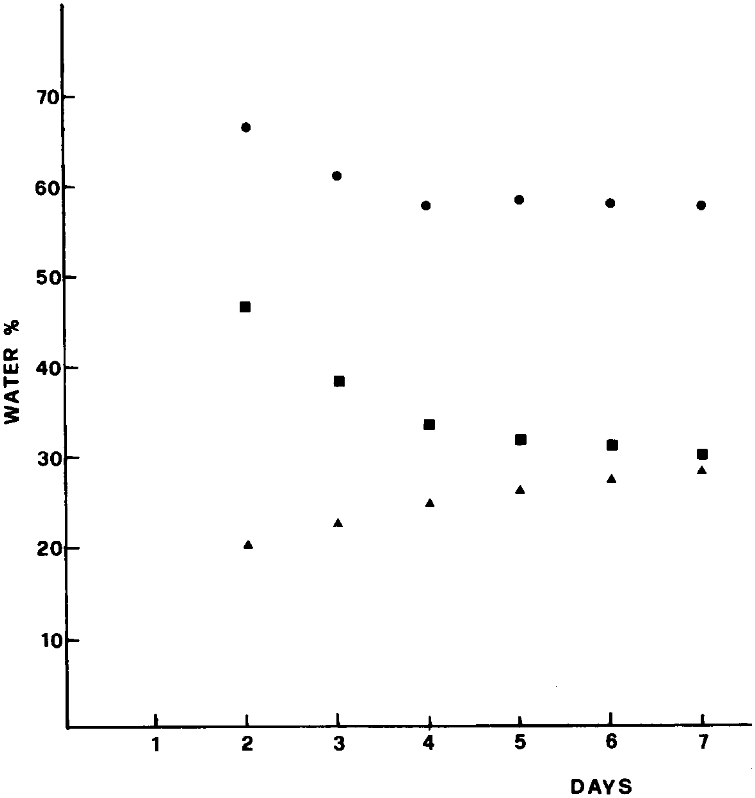

Fig. 13. Plot of the water percentages obtained by thermogravimetry of fiordilatte (sample A) as a function of the ageing time. ●, Total water; ■, Unbound water; ▲, Bound water.

samples of 2 days and 6 days of a fiordilatte of brand A, while Fig. 13 and Table 3 show the data corresponding to the full experiment.

DISCUSSION

TG curves were obtained both in air and oxygen atmosphere. Oxygen gives better results because of the decrease in smoke and sputtering during decomposition of the fats, and, at the same time, the processes of dehydration and of decomposition of the dry cheese are well separated at any of the heating rates used.

As can be seen in Tables 1 and 2, the results obtained by the official methods for the water and for the ashes are always slightly lower than those obtained by thermoanalytical methods.

It is interesting to note that the change in the total water content is mainly due to the variation in the first type of water, that is to say the water not bound to the biological systems, while the bound water, expressed as percent of the dry biological system, appears to be almost constant.

The kinetic studies can explain the differences for the water. Looking at the TG curves for different times, it can be seen that the unbound water is released first and that after four hours it practically disappears. Then the bound water decreases and at twelve hours, in the centre of the sample, about 2% of the water remains, while at the edge there is only 0.9%.

So, using the official method, after twelve hours in an oven at 102 ° C the water is not completely released, a small percentage still remaining in the sample, thus explaining the differences found between the TG and the official method.

The differences in the ashes results can be explained by considering that, in the official method, the sample, in a platinum capsule, must be placed on a water bath for about one hour. Then the capsule is carefully heated to red heat in a Bunsen burner and the flame is removed while the fats are burning. Finally, the sample is calcined at a temperature not higher than 550 ° C.

Even under the best operating conditions this procedure results in sputtering and heavy smoke, caused by the high mass of the sample and the static atmosphere, as well as resulting in a slight loss of sample.

The TG method, using very small samples (maximum 50 mg) in an oxygen flow with a smooth temperature increase, minimizes these problems, thus avoiding sample loss and explaining the differences between the two methods. Moreover the precision of the thermoanalytical technique is higher than that of the official methods. The time required for the thermoanalytical method is very short: about 20 minutes for the analyses of water and ashes working at 40 ° C min^{-1}.

The ageing studies show that while the total water decreases as a function of time as does the unbound water, the bound water, remarkably, increases. This may account for the change in the taste and consistency of aged fiordilatte which becomes less soft and more solid. This is probably due to an increase in the intramolecular bonds which could also explain the change in the shape of the decomposition behaviour.

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